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Phosphate Coatings

PHOSPHATE COATING is the treatment of iron, steel, galvanized steel, or aluminum with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid media, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. The weight and crystalline structure of the coating and the extent of penetration of the coating into the base metal can be controlled by:

- Method of cleaning before treatment
- Use of activating rinses containing titanium and other metals or compounds
- Method of applying the solution
- Temperature, concentration, and duration of treatment
- Modification of the chemical composition of phosphating solution

The method of applying phosphate coatings is usually determined by the size and shape of the article to be coated. Small items, such as nuts, bolts, screws, and stampings, are coated in tumbling barrels immersed in phosphating solution. Large fabricated articles, such as refrigerator cabinets, are spray coated with solution while on conveyors. Automobile bodies are sprayed with or immersed in phosphating solution. Steel sheet and strip can be passed continuously through the phosphating solution or can be sprayed.

Phosphate coatings range in thickness from less than 3 to 50 μm (0.1 to 2 mil). Coating weight (grams per square meter of coated area), rather than coating thickness, has been adopted as the basis for expressing the amount of coating deposited.

Phosphate Coatings

Three principal types of phosphate coatings are in general use: zinc, iron, and manganese. A fourth type, lead phosphate, more recently introduced, is operated at ambient temperatures.

Zinc phosphate coatings encompass a wide range of weights and crystal characteristics, ranging from heavy films with coarse crystals to ultrathin microcrystalline deposits. Zinc phosphate coatings vary from light to dark gray in color. Coatings are darker as the carbon content of the underlying steel increases, as the ferrous content of the coating increases, as heavy metal ions are incorporated into

acid pickled prior to phosphating. Zinc phosphating solutions containing active oxidizers usually produce lighter-colored coatings than do solutions using milder accelerators.

Zinc phosphate coatings can be applied by spray, immersion, or a combination of the two. Coatings can be used for any of the following applications of phosphating: base for paint or oil; aid to cold forming, tube drawing, and wire drawing; increasing wear resistance; or rustproofing. Spray coatings on steel surfaces range in weight from 1.08 to 10.8 g/m² (3.5×10^{-3} to 3.5×10^{-2} oz/ft²); immersion coatings, from 1.61 to 43.0 g/m² (5.28×10^{-3} to 0.141 oz/ft²).

Iron phosphate coatings were the first to be used commercially. Early iron phosphating solutions consisted of ferrous phosphate/phosphoric acid used at temperatures near boiling and produced dark gray coatings with coarse crystals. The term *iron phosphate coatings* refers to coatings resulting from alkali-metal phosphate solutions operated at pH in the range of 4.0 to 5.0, which produce exceedingly fine crystals. The solutions produce an amorphous coating consisting primarily of iron oxides and having an interference color range of iridescent blue to reddish-blue color.

A typical formulation for an iron phosphate bath is (Ref 1):

Component	Composition, %
Phosphate salts	12-15
Phosphoric acid	3-4
Molybdate accelerator	0.25-0.50
Detergents (anionic/nonionic)	8-10

Basically, then, iron phosphate formulations consist of primary phosphate salts and accelerators dissolved in a phosphoric acid solution. It is the acid that initiates the formation of a coating on a metal surface. When acid attacks the metal and begins to be consumed, solution pH at the metal surface rises slightly. This is what causes the primary phosphate salts to drop out of solution and react with the metal surface, forming a crystalline coating.

All iron phosphate conversion coatings are composed of partially neutralized phosphoric acid. But all iron phosphates are not created equal. Other ingredients, such as the specific accelerator used (Table 1), hold part of the key.

Although iron phosphate coatings are applied to steel to provide a receptive surface for the

their chief application is as a base for subsequent films of paint. Processes that produce iron phosphate coatings are also available for treatment of galvanized and aluminum surfaces. Iron phosphate coatings have excellent adherence and provide good resistance to flaking from impact or flexing when painted. Corrosion resistance, either through film or scribe undercut, is usually less than that attained with zinc phosphate. However, a good iron phosphate coating often outperforms a poor zinc phosphate coating.

Spray application of iron phosphate coatings is most frequently used, although immersion application also is practical. The accepted range of coating weights is 0.21 to 0.86 g/m² (6.9×10^{-4} to 0.26 oz/ft²). Little benefit is derived from exceeding this range, and coatings of less than 0.21 g/m² (6.9×10^{-4} oz/ft²) are likely to be nonuniform or discontinuous. Quality iron phosphate coatings are routinely deposited at temperatures from 25 to 65 °C (80 to 150 °F) by either spray or immersion methods.

Manganese phosphate coatings are applied to ferrous parts (bearings, gears, and internal combustion engine parts, for example) for break-in and to prevent galling. These coatings are usually dark gray. However, because almost all manganese phosphate coatings are used as an oil base and the oil intensifies the coloring, manganese phosphate coatings are usually black in appearance. In some instances, a calcium-modified zinc phosphate coating can be substituted for manganese phosphate to impart break-in and antigalling properties.

Manganese phosphate coatings are applied only by immersion, requiring times ranging from 5 to 30 min. Coating weights normally vary from 5.4 to 32.3 g/m² (1.8×10^{-2} to 9.83 oz/ft²), but can be greater if required. The manganese phosphate coating usually preferred is tight and fine-

Table 1 Effect of accelerators on the weight of an iron phosphate coating

Accelerator	Surface treated	Coating weight	
		g/m ²	oz/ft ² $\times 10^{-3}$
Metallic	Steel only	0.11-0.27	0.35-0.88
	Mixed metal loads, ferrous, zinc, and aluminum	0.22-0.38	0.71-1.24
Oxidizer	High-quality steel only	0.43-0.86	1.41-2.82

Table 2 Accelerators used in phosphate coating processes

Type of accelerator	Accelerator source	Effective concentration			Optimum operating conditions					Advantages	Limitations
		%	g/L	lb/gd x 10 ⁻³	Ratio	Temperature °C	°F	Additives			
NO ₃	NaNO ₃ , Zn(NO ₃) ₂ , Ni(NO ₃) ₂	1-3	High NO ₃ :PO ₄ ³⁻	65-93	149-199	...	Lower sludge.	Reduction of FePO ₄ increases the iron content of the coating.	
NO ₂	NaNO ²	...	0.1-0.2	0.8-1.7	NO ₂ :NO = 1:1	(a)	(a)	Continuous	Affords rapid processing even at low temperatures.	Corrosive fumes. Highly unstable at high bath temperatures. Frequent addition is required.	
ClO ₃	Zn(ClO ₃) ₂	0.5-1	(#)	(a)	Continuous	Stable in liquid concentrates. Can be used for bath makeup and replenishment. Overcomes the white staining problem.	Corrosive nature of chlorate and its reduction products. High concentrations poison the bath. Removal of gelatinous precipitate from the resultant phosphate coatings is difficult.	
H ₂ O ₂	H ₂ O ₂	...	0.05	0.4	...	(a)	(a)	...	Low coating weight. No harmful products. Free from staining.	Bath control tends to be critical. Heavy sludge formation. Limited stability. Continuous addition is required. Volatile sludge.	
Perborate	Sodium perborate	(a)	(a)	...	No separate neutralizer is required. Good corrosion resistance.	Continuous addition is required. Volatile sludge.	
Nitroguanidine	Nitroguanidine	55	130	...	Neither the accelerator nor its reduction products are corrosive.	Slightly soluble. Does not control the buildup of ferrous iron in the bath. Highly expensive.	

(a) Low temperature. Source: Ref 3

grain, rather than loose and coarse-grain. However, desired crystal size varies with service requirements. In many instances, the crystal is refined as the result of some pretreatment (certain types of cleaners and/or conditioning agents based on manganese phosphate) of the metal surface.

Manganese-iron phosphate coatings are usually formed from high-temperature baths from 90 to 95 °C (190 to 200 °F).

Composition of Phosphate Coating

All phosphate coatings are produced by the same type of chemical reaction: the acid bath, containing the coating chemicals, reacts with the metal to be coated, and at the interface, a thin film of solution is neutralized because of its attack on the metal. In the neutralized solution, solubility of the metal phosphates is reduced, and they precipitate from the solution as crystals. Crystals are then attracted to the surface of the metal by the normal electrostatic potential within the metal, and they are deposited on the cathodic sites.

When an acid phosphate reacts with steel, two types of iron phosphate are produced: primary phosphate, which enters the coating; and a secondary phosphate, which enters the solution as a soluble iron compound. If this secondary ferrous phosphate were oxidized to a ferric phosphate, it would no longer be soluble and would precipitate from the bath. Oxidizing agents are incorporated to remove the soluble secondary ferrous phosphate because the ferrous phosphate inhibits coating formation.

Although all phosphating baths are acid in nature and to some extent attack the metal being coated, hydrogen embrittlement seldom occurs as a result of phosphating. This is primarily because all phosphating baths contain depolarizers or oxidizers that react with the hydrogen as it is formed

and render it harmless to the metal. In some instances, however, zinc-phosphate processes, intended for use with rust-inhibiting oils for corrosion resistance or manganese-phosphate treatments, can cause hydrogen embrittlement because they may contain a minimum amount of depolarizers and oxidizers. A dwell time before use or mild heating may be needed to relieve embrittlement.

The acidity of phosphating baths varies, depending on the type of phosphating compound and its method of application. Immersion zinc phosphating baths operate in a pH range of 1.4 to 2.4, whereas spray zinc phosphating solutions can operate at a pH as high as 3.4, depending on the bath temperature. Iron phosphating baths usually operate at a pH of 3.8 to 5. Manganese phosphating baths operate in a pH range comparable to that of the immersion zinc phosphating solutions. Lead-phosphate solutions are usually more acidic than any of the others.

Zinc, iron, and manganese phosphating baths usually contain an accelerator, which can range from a mild oxidant, such as nitrate, to one of the more vigorous nitrite, chlorate, peroxide, or organic sulfonic acids (Table 2). The purposes of these accelerators are to speed up the rate of coating, to oxidize ferrous iron, and to reduce crystal size. This is accomplished because of the ability of the accelerators to oxidize the hydrogen from the surface of the metal being coated. Phosphating solution can then contact the metal continuously, permitting completeness of reaction and uniformity of coverage. Accelerators have an oxidizing effect on the dissolved iron in the bath, thus, extending the useful life of the solution. Some zinc and iron phosphating processes rely on oxygen from the air as the accelerator. Zinc phosphating baths for aluminum usually contain complex or free fluorides to accelerate coating formation and to block the coating-inhibiting effect of soluble aluminum.

Applications

On the basis of pounds of chemicals consumed or tons of steel treated, the greatest use of phosphate coatings is as a base for paint. Phosphate coatings are also used to provide:

- A base for oil or other rust-preventive material
- Lubricity and resistance to wear, galling, or scoring of parts moving in contact, with or without oil
- A surface that facilitates cold forming
- Temporary or short-time resistance to mild corrosion
- A base for adhesives in plastic-metal laminations or rubber-to-metal applications

Phosphate Coatings as a Base for Paint

The useful life of any painted metal article depends mainly on the durability of the organic coating itself and the adherence of the film to the surface on which it is applied. The primary function of any protective coating of paint is to prevent corrosion of the base metal in the environment in which it is used. To accomplish this purpose, the method of preparing the metal should reduce the activity of the metal surface, so that underfilm corrosion is prevented at the interface between paint and metal.

When used as a base for paint films, phosphate coatings promote good paint adhesion, increase the resistance of the films to humidity and water soaking, and substantially retard the spread of any corrosion that may occur. A phosphate coating retards the amount of corrosion creep, because the coating is a dielectric film that insulates the active anode and cathode centers existing over the entire surface of the base metal. By insulating these areas, corrosion of the surface is arrested or at least substantially retarded.

PROTECTIVE COATINGS for Metals

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General Introduction

American Chemical Society's Series of Chemical Monographs

By arrangement with the International Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellart Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instru-

iii

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fall in this category. Electrolytic processes, as the name implies, depend on an externally applied voltage to promote the formation of protective films in a suitable electrolyte. The foremost application of this technique is in the anodizing of aluminum alloys. Electrolytic methods are also used for several magnesium treatments.

16. Chemical Conversion and Anodized Coatings

Within recent years protective coatings that are neither of the metallic nor the paint type have come into prominence. They provide an insulating barrier of exceedingly low solubility between a metal and its environment through conversion of the metal surface into a corrosion-resistant, nonreactive form. The conversion consists of a chemical or electrochemical modification of the metal surface so that the coating so formed is an integral part of the parent metal. This is in contrast to paints and most metallic coatings which require no chemical combination with the basis metal. Most of these coatings lend themselves particularly to impregnation with paints, enamels, and lacquers, and it is here that they find their widest applications. The protection provided is enhanced many-fold through improvement of adhesion, restriction of moisture penetration, and prevention of the spread of underfilm corrosion. Most such films are absorbent, providing an ideal base for protective oils and waxes. In some cases conversion coatings are used without further treatments.

The metals for which surface conversion treatments have attained marked commercial significance are iron and steel, zinc, aluminum, brass, and magnesium alloys. To a lesser extent cadmium, tin, copper, brass, and stainless steel are finished in this manner.

The techniques in common use today for forming this type of protective coating fall into two general categories (1) chemical dip, spray, or brush phosphating, used generally to provide a paint base on steel and zinc; and (2) electrolytic methods. In chemical dip reactions an oxidized form of the metal being treated or of a metal ion present in the bath is formed on the metal surface, the operating conditions being controlled to provide the properties required for the intended service. This category includes chromating, of value in protecting zinc and cadmium in humid atmospheres; and chemical oxide coatings, used to enhance the corrosion resistance and appearance of aluminum, steel, and copper alloy parts. Some oxidizing treatments for forming a paint base on magnesium also

PHOSPHATING

Phosphating processes are used to provide protective coatings for a wide variety of iron and steel products. Zinc is also phosphated in commercially significant quantities, and, to a lesser extent, aluminum alloys, cadmium, and tin. For most applications the phosphate coating is not itself sufficiently protective, but serves as an excellent base for impregnation with paint, enamel, lacquer, oil, or wax. Parts which are to be treated with oil or wax are given a thick phosphate coat. Nuts and bolts are illustrative of such articles. The relatively heavy, absorbent coating retains oil for extended periods of time, excluding moisture and providing lubrication. Surfaces that are to be painted are given a "fast" treatment during which a thin phosphate coating is deposited. Here the coating serves to anchor the paint film and suppress corrosion. Phosphating offers the advantage of requiring only simple and relatively inexpensive equipment. Moreover, coating formation depends only on contact between the work and the bath; hence, intricate parts offer no particular problem. The development of "fast" solutions, with treatment times of a minute or less, permits the use of spray application, particularly advantageous in treating bulky articles or in coating composite units after assembly, thus avoiding damage to the coating during assembly.

Historically, phosphating is of ancient origin. There is evidence that the use of phosphates for the protection of certain iron articles was known to the Romans in the third century A.D. In 1869 it was observed¹ that rusting of the metallic parts of women's corsets was retarded by treating them with phosphoric acid. The first important commercial application of phosphate coatings followed the proposal of Coalett in 1908 to treat iron and steel parts in a solution of phosphoric acid and ferrous sulfate in definite proportions.² Later Coalett substituted zinc sulfate for the ferrous sulfate, and in 1918 it was found by the Parker Company³ that

¹ Jacobi, L., "Des Römerkastel Saalburg bei Homburg vor der Höhe," pp. 168, 201, 203, Homburg, 1887; Macchia, O., *Ind. Meccanica*, 17, 617 (1934).

² Turner, H. R., *Monthly Rev. Am. Electropolisher Soc.*, 21, No. 6, 29 (1934).

³ Thornton-Murray, M., *Engineering*, 85, 870 (1908); Blesset, E., *Metal Ind. (N.Y.)*, 9, 207 (1911).

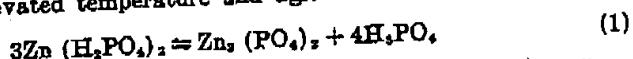
⁴ Chem. & Met. Eng., 18, 264 (1918); Eckelman, L. E., *Chem. & Met. Eng.*, 21, 787 (1919); *Raw Materials*, 5, 438 (1922).

PROTECTIVE COATINGS FOR METALS

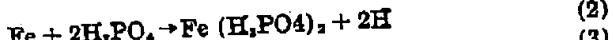
the character of the coating was improved by the use of a solution of primary manganous phosphate. In this process, which came to be known as "Parkerizing," manganese dioxide was added to the bath, it being claimed that oxidation of at least some of the phosphate to the form of ferric phosphate was essential. The time required for treatment was usually from 3 to 4 hours. While the Coalett process known as "Cosletizing" was rather widely used in England for phosphating the steel parts of bicycles and other articles, neither it nor the original Parkerizing process was suited to the needs of the rapidly expanding finishing industry.

The Parker process was improved in 1926 by the adoption of manganese dihydrogen phosphate for the processing solution. This made possible a reduction in time of treatment. Somewhat later a further reduction in processing time to about 10 minutes was effected by incorporating a small percentage of a copper salt in the bath. This permitted the use of the process in a conveyorized or line finishing system.³ The increasing use of phosphate coatings as a base for paint was reflected in the name "bonderizing," given to the improved process.⁴ Still later improvements have been in the direction of time reduction and spray application.

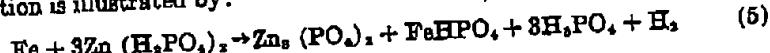
Phosphate coatings consist of crystalline salts of the metal being treated or of metal ions added to the phosphating solution. Although the detailed compositions of phosphate baths are largely proprietary and the exact reactions complex, simple equations may be used to illustrate the formation of the phosphate coatings. A bath commonly used to coat iron or steel is made from primary zinc phosphate in aqueous solution with phosphoric acid which ultimately yields the tertiary salt, a reaction promoted by elevated temperature and agitation.



The bath is so balanced that the tertiary salt is near saturation. Iron, when immersed in such a bath, is attacked by the free phosphoric acid, giving primary and secondary iron phosphate, and liberating hydrogen on cathodic areas.



As the pH at the metal-solution interface is increased, the solubility products of the secondary and tertiary salts are exceeded. The over-all reaction is illustrated by:



³ U. S. Patent 1,888,189.

⁴ Darsey, V. M., *Ind. Eng. Chem.*, 27, 1142 (1935).

CHEMICAL CONVERSION AND ANODIZED COATINGS 547

The crystalline layer formed is largely the insoluble tertiary zinc phosphate, together with a small amount of secondary iron phosphate. Recent evidence indicates that some iron from the solution becomes an integral part of the coating during the process.⁷ The proportion of iron to zinc is dependent on the method of application, solution composition, temperature, and time of processing.

The solution composition is critical in that too much free acid results only in pickling of the steel surface,⁸ while too little promotes sludge formation. This second effect becomes increasingly troublesome as the concentration of ferrous ions in the bath builds up with time. Although it is felt that some iron phosphate is beneficial to the adherence and protective qualities of the coating, excessive amounts are detrimental to corrosion resistance.

A second salt frequently used in phosphating baths is manganese phosphate. The reactions are analogous to those for zinc except that the initial reaction (Eq. 1) yields the secondary as well as tertiary salt.

The coating reaction illustrated above is an extremely slow one, owing largely to cathodic polarization. Accelerating agents are therefore added to the bath to reduce treatment time. Oxidizing agents, such as nitrates, nitrites, or chlorates, behave as depolarizers in oxidizing the hydrogen formed (Eq. 3). Other accelerators for increasing the reaction rate include copper salts, organic compounds such as nitrobenzene, bases such as aniline, toluidene, pyridene, and quinoline. Provided the conditions are so controlled that a fine grain size is obtained, there is no appreciable sacrifice in protective value associated with the use of accelerators. Through the use of accelerators, reaction times have been reduced to less than a minute for paint-base coatings. It has thus become possible to apply phosphate coatings by spray techniques as one step in the conveyor production of large items such as automobile bodies, fenders, etc. The chart in Figure 16-1 summarizes the phosphate treatments in current use together with the basis metals treated and methods and purposes of application.

As in any coating process, the success of the operation depends on proper preparatory surface treatment. Mechanical surface cleaning, such as emery treatment, or blasting with sand, grit, or shot, is employed to remove scale and rust. Degreasing is accomplished with trichloreethylene or in an alkaline bath. Phosphate coatings are particularly sensitive to

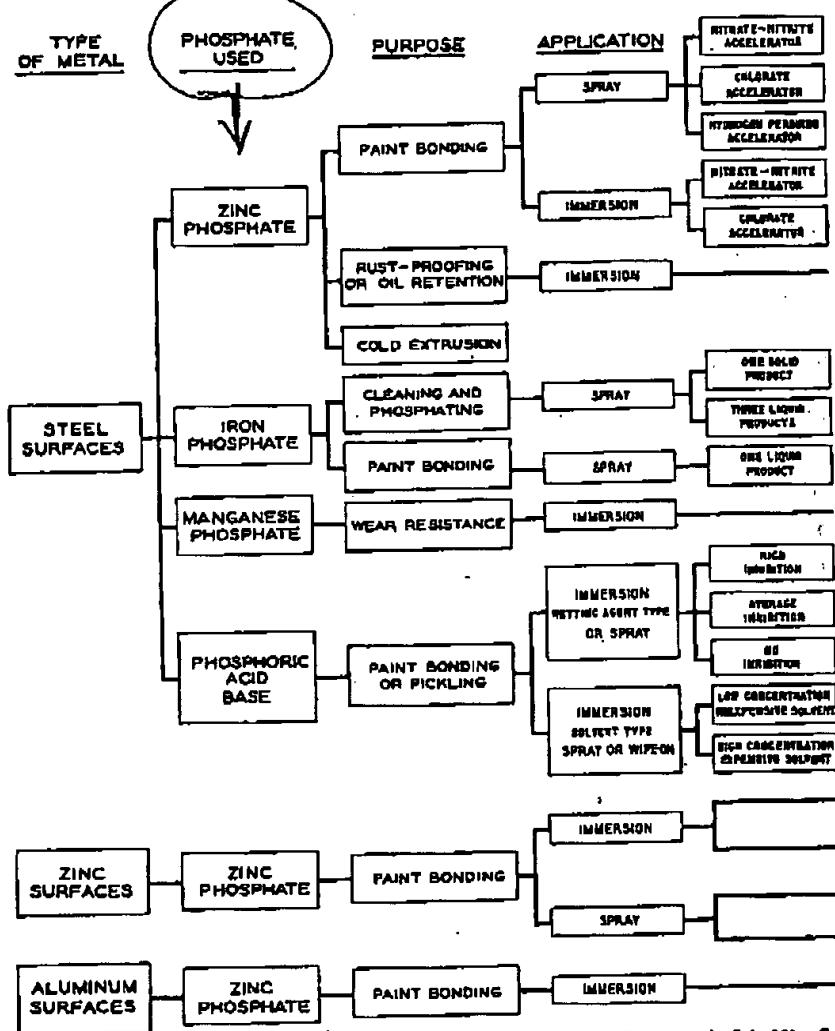
⁷ Eisler, S. L. and Chamberlain, P. G., *Metal Finishing*, 50, No. 8, 113 (1952).

⁸ Phosphoric acid cleaning, as distinguished from a true phosphating treatment, employs a high-acid bath primarily to remove surface dirt and grease, leaving a slight surface etch to promote mechanical bonding with paint, together with a very thin phosphate residue. To insure proper cleaning, the acid concentration must be so high that a substantial crystalline phosphate film cannot be developed.

PROTECTIVE COATINGS FOR METALS

grease, hence parts should not be handled with bare hands after degreasing.

The protective qualities of phosphate coatings are largely a function of the crystalline character of the film, protection increasing with de-



Courtesy of the Pennsylvania Salt Mfg. Co.

Figure 16-1. Summary of types and uses of phosphate coatings.

CHEMICAL CONVERSION AND ANODIZED COATINGS

549

creasing grain size. In general, refinement of the crystalline structure is obtained with increasing temperature. By using suitable addition agents, the temperature can be reduced with no adverse effect on grain size.⁸ Crystal structure is also affected by physical treatment of the surface prior to phosphating. The "wiping" effect, whereby the surface is mechanically wiped prior to treatment, results in refined crystal structure and improved corrosion resistance. This same effect can be approached chemically in a solution containing 1 per cent sodium phosphate and 0.01 per cent titanium as the anhydrous phosphate salt.⁹ The work is predipped in this solution; then, without rinsing, into the phosphate bath. This treatment is applied to both iron and zinc, but primarily to the latter.

Applying phosphate films to ferrous surfaces is an accepted method of reducing wear and galling on mating parts.¹⁰ Properly lubricated, the coating provides myriads of oil reservoirs, effective in reducing friction. Furthermore, the coating is deformed slightly under pressure, thus reducing maximum applied stress. Heavy phosphate films for this purpose are ordinarily formed from "slow" baths of zinc or manganese phosphate at a temperature between 90 and 100°C (200–210°F).¹¹ Reaction times range from 10 to 60 minutes, to produce films of 1000 to 4000 mg per sq ft. There is little dimensional change associated with these coatings; it normally is of the order of 0.005 mm (0.0002 inch) for a heavy coating. Of the many applications of this type, many are found in the automotive industry. Piston rings, rocker arms, camshafts, valves, tappets, and cylinder liners are frequently phosphated to increase life.

The use of zinc phosphate coatings to reduce friction in wire, tube, and deep drawing applications was suggested about twenty years ago, but was not commercially developed until the recent war. Coatings of 150 to 3000 mg per sq/ft are used, the thicker coatings being specified where deformation is light or moderate. For severe forming operations the thickness is limited to preclude injury to the coating. Lubricated coatings of this nature, by markedly reducing friction, reduce wear on dies, permit faster forming operations, and conserve power.¹² No adverse effects on physical properties result from phosphating. Hardness, tensile strength, and temper are unimpaired.

Although the foregoing friction-reducing uses of phosphate coatings are commercially important, the phosphating treatment is known and

⁸ Reeves, M., *Metal Ind. (London)*, 78, 7. (1951).

⁹ Jernstedt, G., *Trans. Electrochem. Soc.*, 83, 381 (1943).

¹⁰ Roosa, M. B., *Lubrication Eng.*, 6, 117 (1950).

¹¹ Ayres, R. F., *Materials & Methods*, 34, No. 4, 100 (1951).

¹² Holden, H. A., *Sheet Metal Ind.*, 26, 123, (1949).

PROTECTIVE COATINGS FOR METALS

used primarily as a paint base for increasing corrosion resistance. The porous nature of the film provides good mechanical anchorage for paint, enamel, or lacquer; the phosphate layer prevents moisture which penetrates the paint film from reaching the basis metal and stifles the spread of corrosion beneath the paint film. These coatings are formed in "fast" zinc or manganese phosphate solutions at temperatures ranging from room temperature to 210°F. Treatment times generally are from 30 seconds to 5 minutes. Coatings range from 100 to 600 mg per sq ft. The risk of corrosion from phosphating solution retained on the treated part varies with the type of solution. Plain metal phosphate-phosphoric acid types are not particularly corrosive, but some of these containing accelerating agents can be quite harmful.¹³ An after treatment in a chromate bath is frequently used to provide added protection. A chromic acid rinse, with acid concentrations up to 0.5 per cent, often proves beneficial, maximum performance being associated with 0.1 to 0.2 per cent. Concentrations greater than 0.5 per cent are injurious because of the dissolving action of the rinsing bath.

Phosphate coatings, being essentially insoluble in most service environments, are protective insofar as they are continuous; continuity, hence, protection, increases with thickness. The corrosion resistance of phosphated but unpainted steel is compared with that of untreated steel in Table 16-1.¹⁴

TABLE 16-1. CORROSION OF PHOSPHATED STEEL (SAE-1020)
COMPARED WITH THAT OF UNTREATED STEEL

Test	Untreated (mg/cm ²)	Phosphated (mg/cm ²)
744 hours in salt fog	24.08	3.22
1 year rural exposure	20.39	1.60

The extent to which phosphate coatings aid in the retention of paint on steel panels is shown in Table 16-2.¹⁵

In addition to increasing adhesion and retention of paints, phosphate coatings also tend to stifle under-film corrosion. A recent six-year test illustrated the protection provided by two spray coats of baked synthetic enamel applied over steel samples treated in three different ways: (1) solvent vapor degreasing, (2) sandblasting, and (3) coating with phosphate. Whereas underfilm and general corrosion were evident on the first

¹³ Clarke, S. G., and Longhurst, E. E., *J. Iron Steel Inst. (London)*, 170, 15 (1952).

¹⁴ Darsay, V. M., and Cavanaugh, W. R., Parker Rust Proof Co., *Trans. Electrochem Soc.*, 91, 351 (1947).

¹⁵ Darsay, V. M., Parker Rust Proof Co., "Phosphate Coatings," Reprinted with permission from "Corrosion Handbook," edited by H. H. Uhlig, p. 887, New York, John Wiley & Sons, Inc., 1948.

CHEMICAL CONVERSION AND ANODIZED COATINGS 551

two surfaces, the phosphate coating improved paint protection and retarded underfilm attack.¹⁶

The affinity of phosphate coatings for oil and wax is exploited in rust-proofing many articles. The adhesion and abrasion resistance of the coating is such that threaded articles, such as nuts, bolts, and screws, can be

TABLE 16-2. RETENTION OF PAINT BY UNTREATED AND PHOSPHATE-COATED STEEL

	Primer Wt. Retained (oz/ft ²)	Increase in Retention Over Untreated Steel (%)
Steel untreated	0.139	—
Steel-phosphate coated Roller application	0.177	27.3
Steel-phosphate coated By spray	0.200	48.9
Steel-phosphate coated By immersion dipping	0.242	74.0

so treated. During World Wars I and II small arms were rustproofed by phosphating, then treating with chromic acid and a rust-preventive oil. The corrosion protection obtained is indicated in Table 16-3,¹⁶ in which are listed salt-spray requirements for military equipment finished in this manner.

TABLE 16-3. SALT SPRAY RESISTANCE OF PHOSPHATED STEEL BEFORE AND AFTER OILING

Class	Coating Wt. (mg/ft ²)	Salt Spray Resistance (hours)	
		Before	After
A	1000-4000	1	24
B	1000-4000	.2	36

Besides iron and steel, other metals, notably zinc and aluminum, are phosphate treated on a large scale. Zinc surfaces which are painted with no intermediate treatment provide inadequate service due primarily to the reaction of zinc with the paint vehicle. Zinc soaps are formed, destroying the bond between the paint and the zinc. Phosphating is one treatment used to avoid this difficulty, and also to increase the mechanical anchorage of the paint. Cadmium is treated in the same way. The baths are of zinc phosphate in which the work is dipped for about 2 minutes, forming a film of 75 to 200 mg per sq ft.¹⁷ Phosphating is recommended frequently for zinc- or cadmium-plated steel that is to be painted. Zinc-flash bonderizing consists in applying a thin electrodeposit of zinc which is given a phosphating treatment, then painted. This composite coating provides a higher degree of corrosion protection to iron or steel than does normal phosphating and painting. The zinc thickness is

¹⁶ Gentieu, N. P., *Machine Design*, 24, No. 2, 141 (1952).

¹⁷ Douty, A., *Plating*, 38, 1031 (1951).

652

PROTECTIVE COATINGS FOR METALS

usually 0.0006 to 0.0015 mm (0.00025 to 0.0006 inch) for indoor and 0.0025 to 0.0035 mm (0.0010 to 0.0015 inch) for outdoor exposure.

For treating tin a special technique is available called "Protecta Tin" in which an oxide and phosphate complex are formed on the tin, imparting an increased resistance to corrosion and to staining by sulfur products.¹² Processing is carried out by immersion for less than 30 seconds at 85°C in a solution containing 9 pounds trisodium phosphate (anhydrous), 8 pounds sodium dichromate, 20 pounds sodium hydroxide, 3 pounds wetting agent, and water to make 121 gallons.¹³ The treatment does not affect the appearance of the metal nor does it interfere with subsequent lacquering or lithographic printing. This process is used to increase the shelf-life of canned foods both by retarding rusting of the outside of the can during storage in damp conditions, and by preventing the unsightly blackening of can interiors resulting from sulfur originating in meat, fish, soup, and many vegetables.

CHROMATE COATINGS

Chromate conversion coatings were widely used during World War II for protection of zinc- and cadmium-plated parts in tropical service. Since that time they have undergone marked commercial development, and are now firmly established in the metal finishing field. They are used purely for protection purposes without additional finishing treatment, or they may be finished with lacquer or paint to combine protection with product appearance. Their use has been extended to the protection of zinc-base die castings and aluminum.

Zinc, when exposed to conditions that give rise to moisture condensation, develops a bulky white corrosion product. This most readily occurs in highly humid conditions such as prevail in the tropics or the Gulf Coast where the daily temperature variation causes intermittent condensation or dew formation. Storage of zinc or zinc-coated parts in unheated warehouses during periods of high humidity or the packaging of such products in boxes made of unseasoned wood or damp paper stock has caused corrosion of this "white bloom" type. In addition to detracting from the appearance of the part, these corrosion products can impair the operation of certain types of equipment, such as relays and switches. It is for such applications that chromate coatings are largely employed to retard the corrosion of zinc and cadmium plated parts and zinc-base die castings.

Applications of chromate coatings are predominantly by immersion

¹² Kerr, R., *J. Soc. Chem. Ind.*, 65, 101 (1946).

¹³ *Product Finishing (London)*, 3, No. 12, 55 (1950).

CHEMICAL CONVERSION AND ANODIZED COATINGS 553

processes, although electrolytic methods are used to some extent in the aircraft industry. The bath compositions are largely proprietary but all contain two basic constituents: hexavalent chromium ions and a mineral acid. Some also contain one or more organic acids. On immersion, the zinc or cadmium article is attacked by the mineral acid with an attendant rise in pH of the solution next to the metal. At the same time some hexavalent chromium is reduced to the trivalent state. At a critical pH the trivalent chromium and some hexavalent chromium are coprecipitated on the metal surface.

One of the oldest and still popular chromating processes is known as the "Cronak"²⁰ process²⁰ concerning which details have been published.²¹ The bath contains chiefly sodium dichromate in fairly high concentrations, slightly acidified with sulfuric acid. Analytical studies indicate the film formed from this bath to be a basic chromium chromate of the general formula $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_4 \cdot x\text{H}_2\text{O}$. A typical film, dried at 110°C (230°F), has been analyzed as follows:

Hexavalent chromium	8.68%
Trivalent chromium	28.2%
Sulfate	3.27%
Zinc	2.12%
Sodium	0.23%
Water	19.2%

← NO
FLASH
!!

The thickness is about 0.0005 mm (0.00002 inch).

Chromate films are generally noncrystalline, nonporous, and gel-like. They are quite susceptible to damage from abrasion immediately following film formation; hence should be aged 12 to 24 hours, before being subjected to normal shop handling. Electrolytically applied coatings are not subject to this limitation.

Chromate films which provide maximum protection contain both trivalent and hexavalent chromium.²² Protection is provided in two ways. The nonporous nature of the film physically excludes, to a large extent, moisture from the metal. At discontinuities in the film, the hexavalent chromium, being slightly soluble, exerts its well-known inhibiting action. Experiments show that the formation of white corrosion product is inhibited so long as a minimum amount of hexavalent chromium remains in the film. The useful life of a chromated part thus depends on the rate at which hexavalent chromium is leached from the film, i.e., on the degree of wetting of the part. The protection provided by a Cronak coating in stagnant water is illustrated in Table 16-4.²³

²⁰ Registered trade mark of New Jersey Zinc Company.

²¹ U. S. Patent 2,035,280 (Mar. 24, 1936) E. J. Wilheim (to New Jersey Zinc Co.).

²² Anderson, E. A., *Proc. Am. Electroplaters' Soc.*, 30, 8 (1943).

²³ Ostrander, C. W., *Plating*, 38, 1039 (1951).

3200

Chemical Abstracts

Vol. 26

ZnI_4 m. 132-3°; $(Et_4S)_2ZnI_4$ m. 149°; $(Et_4MeS)_2ZnI_4$ m. 173-4°; $(Et_4PrS)_2ZnI_4$ m. 148°.

ALFRED HOFFMANN

Composition of complex metal cyanide radicals. Complex Ni cyanide radical (MASAKI) 2. Synthesis and x-ray investigation of $NiCr_2O_4$ (HOLGERSSON) 2.

LAFUMA, HENRI: Recherches sur les aluminaux de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium. Paris: Vuibert. 08 pp. F. 16.

7--ANALYTICAL CHEMISTRY

W. T. HALL

An improved method of quantitative spectrographic analysis. C. C. NITCHIE AND G. W. STAMOSN. *Ind. Eng. Chem., Anal. Ed.* 4, 182-85 (1932).—The method employed is a modification of the methods of Gerlach and Schweitzer and N. (C. A. 23, 1587). In the improved method an addnl. element is added to the sample in a const. known amt. for comparison purposes. The use of a recording microphotometer is now justified and considerable time is saved. Four requirements are listed for satisfactory comparison of spectral lines. App. and procedure are described, and spectra and microphotometric records are shown. Concrete examples are given and the errors are analyzed. The deviation from the mean of 4 detns. is 1 part in from 10 to 20. H. A. S.

Micro-alkalimetry and acidimetry. S. K. CHIKKOV. *Bull. inst. recherches biol. Perm* 7, No. 7/8, 427-40 (German summary) 440-1 (1931).—The soln. to be investigated is titrated to the intermediate color of a 2-color indicator, with not stronger than 0.01 *N* reagents from a membrane microburet. Formulas are given for calcg. the decrease in acidity or alkyl. p_K values are taken from tables. R. H. FERGUSON.

Thermometric titration. TAKAYUKI SOMIYA. *J. Soc. Chem. Ind.* 51, 135-40T (1932); cf. C. A. 23, 1425, 2030; 23, 1840, 2907, 4907, 4908; 24, 3389, 3915.—The necessary app. is shown and numerous applications of the method are described.

W. T. H.

Use of benzidine acetate as indicator in molybdo-manganimetry; application to the electrolytic determination of a few hundredths of a milligram of copper. R. GUILLERMET AND L. THIVOLLE. *Compt. rend. soc. biol.* 108, 30-2 (1931).—Fontés and Thivolle (C. A. 17, 1199) developed a method for detg. Cu which depended upon the fact that when Cu is plunged into a phosphomolybdate reagent (boil 40 g. of NH_4 molybdate, 60 cc. of NaOH soln., d. 1.36, and 100 cc. of water until no more NH_3 is evolved, cool, add 200 cc. of water and 200 cc. of H_3PO_4 , d. 1.30, boil 15 min., cool and dil. to 1 l.) the Cu dissolves, forming a blue soln. which becomes colorless when titrated with $KMnO_4$. To overcome the difficulty in detg. the end point, it is now recommended to use benzidine acetate soln. as indicator. Dissolve 1 g. of benzidine in 10 cc. of glacial AcOH, boil and dil. to 100 cc. After washing an electrolytic Cu deposit, plunge the electrode into enough of the phosphomolybdc reagent to cover it (3 cc. in a small tube with a Pt wire cathode), allow the color to develop for a few min., while using the cathode as a stirrer and titrate with dil. $KMnO_4$ after adding the indicator. W. T. H.

A neutral buffered standard, for hydrogen-ion work and accurate titrations, which can be prepared in one minute. ROGER J. WILLIAMS AND CARL M. LYMAN. *J. Am. Chem. Soc.* 54, 1911-2 (1932).— NH_4OAc solns. through wide limits of concn. have a p_H of almost exactly 7.00. W. T. H.

New reagent for the detection of hydroxy acids. C. H. LIBERALI. *Bol. assoc. brasili. pharm.* 12, No. 10, 24 (1931).—Hydroxy acids can be detected by the use of the following reagent: $FeCl_3$ (10%) 32.4 cc., KCNS (10%) 58.2 cc., H_2O to 100 cc. The reagent turns yellow on the addn. of a neutral soln. of hydroxy acid. AcOH and oxalic acid also give the same color. Addn. of 1 drop of HNO_3 brings back the original red color with hydroxy acids. With AcOH and oxalic acids the color does not return. E. S. G. B.

Preparation of sodium cobaltinitrite as potassium reagent. E. RUPP AND A. FOGGENDORF. *Apoth. Ztg.* 47, 282-3 (1932).—To 5 g. of powd. $Co(NO_3)_2$ in 2.1 g. AcOH and 1 g. H_2O add a luke-warm soln. of 10 g. $NaNO_3$ in 11 g. H_2O , remove the N_2O_4 by a 30-min. current of aspirated air through the mixt., allow to stand 15-30 min., pass through a filter to remove any turbidity and mix in a porcelain mortar with 20 g. of pure, freshly dehydrated Na_2SO_4 , then place in a vacuum desiccator for a day. Triturate the golden yellow cryst. mass and preserve in amber glass. W. O. E.

exchanged at once. Fe^{2+} and FeY^- , both 0.0125 M, at pH from 1.6 to 5.0 showed an immediate partial and very slow subsequent exchange. Temp. = 25°. Tracers were Co^{2+} , Fe^{2+} , and Ni^{2+} . Cf. C.A. 42, 1523s. P. E. B.

New approaches to the study of the reaction between a potassium and cobaltinitrite ions. Angel del Campo, Vicente Boissier, and Angel Hoyos (Univ. Madrid). *Rev. real acad. cienc. exactas y nat. Madrid* 34, 353-89 (1940).— $\text{K}_3\text{Co}(\text{NO}_3)_6$ was pptd. with stirring by adding DeKoninck's reagent (C.A. 3, 1628, (1909)) to a known soln. of KCl , filtering, drying in a current of air at 100°, and weighing in a tared filter crucible. The wt. of ppt. is less when the soln. is stirred during pptn.; hence adsorption takes place. On long standing, with the ppt. in contact with an excess of $\text{Na}_3\text{Co}(\text{NO}_3)_6$, the wt. increases considerably; Na probably substitutes for K in the ppt., as evidenced by qual. analysis. The ppt. is probably a mixt. of $\text{K}_3[\text{Co}(\text{NO}_3)_6]\cdot\text{H}_2\text{O}$ and $\text{K}_2\text{Na}[\text{Co}(\text{NO}_3)_6]$, but the K is nevertheless pptd. quant. K, pptd. with $\text{Li}_3[\text{Co}(\text{NO}_3)_6]$, can be filtered and washed more easily than when pptd. with the Na reagent, and comes down as well-formed cubic crystals corresponding closely to the formula $\text{K}_2[\text{Co}(\text{NO}_3)_6]$ when an excess of reagent is employed; the wt. of the ppt. is almost independent of whether or not the soln. is agitated during pptn., in contrast to the large changes observed with the Na reagent. The anion of the K soln. has no effect. R. L. Wolke

Chemistry of thorium in aqueous solutions. I. Organic and inorganic complexes. R. A. Day, Jr., and R. W. Stoughton (Oak Ridge Natl. Lab., Oak Ridge, Tenn.). J. Am. Chem. Soc. 72, 5682-7 (1950).—Equil. consts. for the formation of complex ions of Th with the anions of HF , H_2O , Cl_3COOH , HBrO_3 , Cl_3CHCOOH , HNO_3 , HCl , and ClCH_2COOH in aq. soln. with a H-ion concn. of 0.5 M and an ionic strength of 0.5 were obtained by detg. the distribution ratios between the aq. soln. and benzene contg. the monofluoroacetone (I) as a chelating agent. The consts. for the 1:1 complexes decrease in the order of the above listing, going from 4.3×10^4 for ThF^{4+} to 1.33. Higher complexing corresponding to Th/anion ratios of 2 and 3 was

found for the first five anions in the list; the corresponding consts. are presented. Evidence was found for the existence of double complexes of the type $\text{Th}(\text{NO}_3)_3\text{F}^{4+}$ and $\text{Th}(\text{NO}_3)_3\text{F}^{+}$ in mixts. of HNO_3 and HF. Acetic acid in the aq. phase increases the extractability of the chelated product formed between Th and (I). J. Van Wazer

Sequestering properties of salicylic acid. Complexes of sulfosalicylic acid. Giovanni Mannelli. Ann. chim. applicata 38, 594-601 (1948).—Fe is sepd. from Ti by treating a soln. of the sulfates with NH_3 salicylate (I) and $(\text{NH}_4)_2\text{CO}_3$, followed by pptn. of Fe with H_2S . Addn. of aq. NH_3 and boiling then gives TiO_2 . Fe is sepd. from Mn, with I, the Mn being pptd. as phosphate, and similarly Fe from Ti, the Ti being pptd. as chromate in presence of I. Na sulfosalicylate and $\text{Be}(\text{OH})_2$ give Na_2Be sulfosalicylate, $\text{Cu}_{1-\text{x}}\text{Hg}_{\text{x}}\text{O}_{1-\text{x}}\text{S}_{\text{x}}\text{Na}_2\text{Be}$; similarly are formed Na_2UO_2 sulfosalicylate, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_{\text{x}}\text{Na}_2\text{U}$ (+4 H_2O), and K_2Ni sulfosalicylate, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_{\text{x}}\text{K}_2\text{Ni}$. B. A.

Electrochemical study of complexes of the silver ion and amino dicarboxylic acids. Suzanne Valladas-Dubois. Compt. rend. 231, 1209-1300 (1950).—Aspartic acid and glutamic acid, like glycine, at high pH form complex anions of about the same stability, corresponding to 2 mol. of the amino acid to one of AgNO_3 . Earl S. McCollum

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7—ANALYTICAL CHEMISTRY

W. T. HALL

History of analytical chemistry in Russia. K. B. Vatsinskii. *Uspekhi Khim.* 18, 623-8 (1949). N. Thon

Recent developments in inorganic analytical chemistry. J. C. Geertsma. S. African Ind. Chemist 2, 31-3 (1948).—A description is given of (1) the use of the Walden Ag reductor and internal indicators in the detn. of Fe with $\text{K}_2\text{Cr}_2\text{O}_7$, (2) detn. of C in presence of large aints. of S, e.g., coal in pyrites concentrates, with MnO_2 on pumice granules to absorb the SO_2 and SO_3 , and (3) detn. of CO_2 in solid materials. B. A.

Analytical methods for determining the concentration of ionically active substances. H. Schwerdtner (Chemnitz, Ger.). Chem. Tech. (Berlin) 2, 361-4 (1950).—A review. Paul W. Hawerton

Qualitative analysis without hydrogen sulfide. X. Reduction method. Toshiyasu Kiba (Kanazawa Univ.) J. Chem. Soc. Japan, Pure Chem. Sect., 70, 145-7 (1949); cf. C.A. 43, 2813c.—Metallic Zn can be used as a group reagent to sep. ions from acidic soln. Systematic procedures of group sepa. and identification of ions are given in tables. K. Yamasaki

Fluorimetric analysis with morin. E. V. Rouir and H. Dietz (Atelier construct. elec. Charleroi, Charleroi, Belg.). Congr. groupement avancé. méthod. anal. spectrograph. produits mél. 12, 149-55 (1949).—Al reacts with morin to produce a fluorescence which served as a means of detg. 0.001-9% Al in bronzes and brasses. For less than 1% Al the relative error was between ± 5 and 7.5%; for higher percentages, $\pm 2\%$. Other metals causing interference in the analysis were removed by electrolysis. M. A. R.

Quantitative analysis of powders by infrared spectrometry. Georges Pilat (Univ. Liège). Bull. soc. chim. Belges 59, 527-51 (1950); cf. C.A. 43, 7266h.—The compensated extinction coeff. method, detd. with an internal standard, is applied to the analysis of powders when Beer's law does not hold, and when there is overlapping between the absorptions of the components of the mixt. Results are given for the analysis of mixts. of cinchonidine, cinchonine,

quinidine and quinine; and of leucine, norleucine, and iso-leucine. H. N. Dyer

Spectrochemical analysis of a solution on graphite. M. van Doorselaer, J. Eeckhout, and J. Gillis (Univ. Ghent, Belg.). Congr. groupement avancé. méthod. anal. spectrograph. produits mél. 12, 51-7 (1949).—Factors which affected bronze analysis according to the method of Rivas (cf. C.A. 32, 16011) were studied. When adsorption of the soln. on graphite took place at a temp. above 100°, the sensitivity of spectral lines was at a max. and their relative intensities were const. An increase in the concn. of the soln. gave a greater sensitivity, except in the case of some elements such as Al, but did not influence the relative intensities. The effect of the vol. of the soln. on the electrode was negligible. A change in the apion ratio of a soln. produced changes in the spectra because of differences in the volatility, as well as adsorption and absorption characteristics of various salts and their complexes. The presence of colloidal Sm gave abnormally high results. M. A. Rinehart

Amperometric titration of sulphydryl groups: microgram analysis. Sheldon Rosenberg, J. C. Perrone, and Paul L. Kirk (Univ. of California Med. School, Berkeley). Anal. Chem. 22, 1186-7 (1960).—The argentometric procedure of Kolthoff and Harris (C.A. 44, 76a) is modified. A vibrating Pt electrode is used as a combination electrode-stirrer, and the titrating soln. is added from a horizontal microburet. For γ aints. of cysteine-HCl and glutathione the error was less than 5% in all cases. Titration of denatured bovine serum albumen should approx. 0.3% sulphydryl (as cysteine); this value was essentially independent of the nature of the denaturing agent. T. H. Dunkelberger

Utilization of ion exchangers in analytical chemistry. XVI. Gunnar Gabrielsson and Olof Samuelson (Chalmers Tek. Högskola, Göteborg, Sweden). Svensk Kem. Tid. 62, 214-20 (1950) (in English); cf. C.A. 44, 6769f.—Aldehydes may be retained quantitatively by an ion exchanger in the bisulfite form. The break-through curves have the same shape as those obtained for inorg. acids, showing that the

Inorganic Syntheses

Volume II

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The precipitate is finally washed with 12-l. portions of water, centrifuged, and dried at 110° in an electric oven. A yield of 35 g. of the hydrous β-1-hydrate is obtained from 100 g. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The process of settling in the later stages is very slow and much time may be saved by the use of a centrifuge.

Analysis

The amount of chloride in the sample is determined by dissolving a weighed portion in warm, concentrated nitric acid. After evaporation to remove excess acid and dilution with water, the chloride is precipitated as silver chloride, dissolved in ammonia, reprecipitated with dilute nitric acid, and weighed in the usual manner. The iron(III) in the combined filtrates is determined by precipitating with ammonia and is weighed as Fe_2O_3 according to the standard procedure. Typical analytical results give an Fe:Cl ratio of 40:1.

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69. HEXAMMINECOBALT(III) SALTS*

SUBMITTED BY JANNEK BJERRUM† AND JAMES P. McREYNOLDS‡
CHECKED BY ALFRED L. OFFORD§ AND R. W. PARKER§

Hexamminecobalt(III) salts may be prepared by any of three methods that depend on oxidation of cobalt(II) ion

* Procedures for preparing most of these salts were originally submitted by Dr. McReynolds, who was impressed by the simplicity of Dr. Bjerrum's method. Shortly after the manuscript for Vol. II had been sent to the publisher, similar procedures for three of these salts were submitted by Dr. Bjerrum. Inasmuch as the method was developed by Dr. Bjerrum and war conditions prevented his submitting his procedures at an earlier date, the editors have taken the liberty of combining the two sets of directions and presenting them as a joint effort of the two men.

† University of Copenhagen, Copenhagen, Denmark.

‡ The Ohio State University, Columbus, Ohio; deceased.

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HEXAMMINECOBALT(III) SALTS

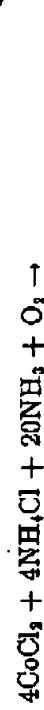
217

in ammoniacal solution: (1) air oxidation, with formation of the pentammine ion, which is converted to the hexamine by heating with aqueous ammonia under pressure;^{—s, 1)} (2) oxidation with an agent such as hydrogen peroxide,⁴ iodine,⁵ potassium permanganate,⁶ lead dioxide,⁷ or hypochlorite solutions;⁸ (3) oxidation in the presence of a catalyst that allows equilibrium between the pentammine and hexamine ions to be established at room temperature and atmospheric pressure. These compounds may also be prepared indirectly from other hexamminecobalt(III) salts.^{9, 10}

In the best of the catalytic methods diamminesilver ion,^{11, 12} or decolorizing charcoal¹³ is used as a catalyst. The method devised by J. Bjerrum¹⁴ in which decolorizing charcoal is the catalyst is simple, gives high yields of pure product, and is not time-consuming. A high concentration of ammonium salt is sufficient to stabilize the hexamminecobalt(III) ion, and the carbon serves only to establish the equilibrium. Air is used as oxidant except when the cobalt(II) compound is slightly soluble in the ammoniacal solution, as in the preparation of $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, for which hydrogen peroxide is preferable.

Procedure

A. HEXAMMINECOBALT(III) CHLORIDE



Two hundred and forty grams (1 mol) of cobalt(II) chlorides 6-hydrate and 160 g. (3 mols) of ammonium chloride are added to 200 ml. of water. The mixture is shaken until most of the salts are dissolved. Then 4 g. of activated decolorizing charcoal¹³ and 500 ml. of concentrated ammonia are added. Air is bubbled vigorously

* In order to obtain a rapid reaction, care must be exercised in the choice of this catalyst. Charcoal from the center of a package has been found to be much more effective than that from the top.

218 INORGANIC SYNTHESSES

through the mixture until the red solution becomes yellowish brown (usually about 4 hr.).* The air inlet tube is of fairly large bore (10 mm.) to prevent clogging with the precipitated hexamminecobalt(III) salt.

The crystals and carbon are filtered on a Buchner funnel and then added to a solution of 15 to 30 ml. of concentrated hydrochloric acid in 1500 ml. of water; sufficient acid should be used to give the entire mixture an acid reaction. The mixture is heated on a hot plate to effect complete solution and is filtered hot. The hexamminecobalt(III) chloride is precipitated by adding 400 ml. of concentrated hydrochloric acid and slowly cooling to 0°. The precipitate is filtered, washed first with 60 per cent and then with 95 per cent alcohol, and dried at 80 to 100°.[†] Yield 230 g. (85 per cent). *Anal.* Calcd. for [Co(NH₃)₆]Cl₃: Co, 22.0; Cl, 39.8; NH₃, 38.2. Found: Co, 22.0; Cl, 39.8; NH₃, 38.1.

B. HEXAMMINECOBALT(III) NITRATE

1. 4Co(NO₃)₂ + 20NH₃ + O₂ → 4[Co(NH₃)₆]([NO₃]₆) + 2H₂O
 2. [Co(NH₃)₆]Cl₃ + 3HNO₃ → [Co(NH₃)₆]([NO₃]₆) + 3HCl

Method 1. Seventy-three grams of cobalt nitrate 6-hydrate (0.25 mol) is dissolved in 100 ml. of water, and, in the order mentioned, 80 g. (1 mol) of ammonium nitrate, 2 g. of activated charcoal, and 180 ml. of concentrated ammonia (about 2.5 mols of NH₃) are added. The solution is oxidized by air as specified in Procedure A. The salt is washed with a little ice-cold water and is dissolved on a steam bath in 1300 to 1500 ml. of water containing enough nitric acid to give the mixture an acid reaction. After

* Care should be taken that the bubbling is not too vigorous, as this removes part of the ammonia from the solution. If this happens, the solution stays red instead of becoming yellow. Although more ammonia may be added, the yield will be decreased somewhat.

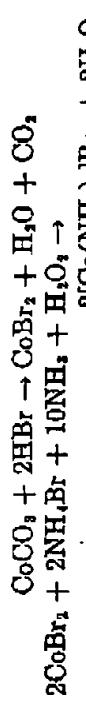
† When the salt is dried at a higher temperature, it sometimes turns green. The original color is restored by redissolving and reprecipitating with hydrochloric acid.

HEXAMMINECOBALT(III) SALTS 219

removal of the carbon by filtration, the solution is treated with 200 ml. of concentrated nitric acid and left to cool. The precipitated salt is washed with water and alcohol and dried at 100°. Yield 77 to 79 g. (88 to 90 per cent). *Anal.* Calcd. for [Co(NH₃)₆]([NO₃]₆): Co, 17.0; NH₃, 29.4. Found: Co, 16.9; NH₃, 29.4.

Method 2. The precipitate from the oxidation of cobalt(II) chloride (Procedure A) is dissolved in 1500 ml. of water containing 15 to 30 ml. of concentrated nitric acid. The carbon is removed and the salt precipitated with 450 ml. of concentrated nitric acid. The crystals are washed with two 200-ml. portions of alcohol to remove excess acid and dried at 100°. Yield 103 g. (88 per cent). A solution of these crystals gives only a slight turbidity with silver nitrate.

C. HEXAMMINECOBALT(III) BROMIDE



Twenty-four grams (0.20 mol) of cobalt carbonate* is added slowly to 100 ml. of 45 per cent hydrobromic acid (0.80 mol). To the solution, 2 g. of activated charcoal and 120 ml. of concentrated ammonia (1.6 mols of NH₃) are added. The precipitate of cobalt(II) salt that appears is disregarded, and 40 ml. of 30 per cent hydrogen peroxide (0.40 mol) is added slowly while the solution is stirred. When the vigorous effervescence has ceased, the main part of the cobalt(II) precipitate has been converted into the desired product. To complete the equilibrium adjustment, the mixture is heated for 5 min. on a steam bath and then left standing for ½ hr. The salt-carbon mixture is filtered, washed with a little cold water, and treated with 900 to 1000 ml. of water containing sufficient

* A cobalt determination must be made on the cobalt carbonate used if an accurate check on the yield of the complex salt is desired.

Inorganic Syntheses

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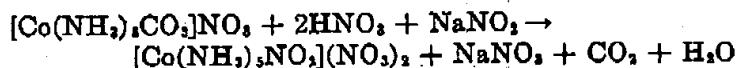
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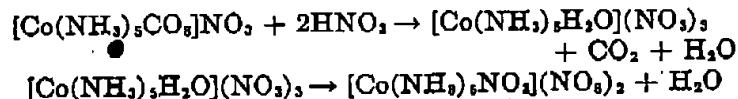
grinding procedure is repeated. The residue is again collected on a filter and washed with cold water until the filtrate is no longer orange, but instead is faintly greenish. The salt is finally washed with methanol and ether and dried at 50°. Yield, 7.8 g. (86%). *Anal.* Calcd. for $[\text{Co}(\text{NH}_3)_6\text{I}](\text{NO}_3)_2$: NH_3 , 21.8. Found: NH_3 , 21.8.

D. NITROPENTAMMINECOBALT(III) NITRATE⁴



Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is suspended in 25 ml. of water, and 10 g. of sodium nitrite (0.14 mol) and 10 ml. of colorless nitric acid (1:1 concentrated acid and water) are added. The mixture is stirred for 15 minutes at room temperature, and then 200 ml. of methanol is added to the slurry. The precipitate is collected on a filter, washed with methanol and ether, and dried at 50°. Yield, 10 g. (88%). *Anal.* Calcd. for $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$: NH_3 , 27.1. Found: NH_3 , 27.1.

E. NITRATOPENTAMMINECOBALT(III) NITRATE⁵



Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is suspended in 25 ml. of water, and 20 ml. of colorless nitric acid (1:1 concentrated acid and water) is added with stirring. When the evolution of carbon dioxide has stopped (10 minutes), 100 ml. of methanol is added, the aquopentammine cobalt(III) nitrate is collected on a filter, and washed with alcohol and ether. This salt is heated at 100° for 18 hours (until 1 mol of water is lost), yielding 10 g. (83%) of the desired material. *Anal.* Calcd. for $[\text{Co}(\text{NH}_3)_5\text{NO}_4](\text{NO}_3)_2$: NH_3 , 25.8. Found: NH_3 , 25.6.

Inorganic Syntheses

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CARBONATOTETRAMMINECOBALT(III) NITRATE 173

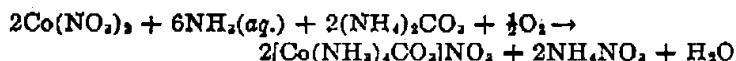
safety trap and into a beaker of water where the acid is titrated with 2 *N* sodium hydroxide solution.

The mixture is stirred at a rapid rate and heated for 30 minutes to 126°, whereupon the black slurry thickens. Only approximately 1 ml. of the sodium hydroxide is consumed in this initial heating. The reaction is then allowed to proceed rapidly at 128 to 139° for 2 hours. In the course of the reaction the mixture becomes light tan and appreciably less viscous, and the theoretical amount of sodium hydroxide is required to neutralize the hydrogen chloride which is evolved. Very little additional hydrogen chloride is liberated during another hour of heating.

The solid is filtered, washed repeatedly with chloroform or benzene, and dried *in vacuo*; the yield is 99%. *Anal.* Calcd. for FeCl₂: Fe, 44.06. Found: Fe, 43.89.

References

1. P. KOVACIC and N. O. BRACE: *J. Am. Chem. Soc.*, **76**, 5491 (1954).
2. N. O. BRACE: U.S. patent 2,719,074 (1955).

**55. CARBONATOTETRAMMINECOBALT(III)
NITRATE**

SUBMITTED BY G. SCHLESSINGER*

CHECKED BY JOHN W. SIMMONS,† GERHARDT JABS,† AND MARK M. CHAMBERLAIN†

The first salts of this series were prepared by Vortmann¹ and later extensively investigated by Jørgensen,² who, however, gave only semiquantitative synthetic preparations.

* University of Pennsylvania, Philadelphia, Pa.

† Western Reserve University, Cleveland, Ohio.

The method given below, which is a more exact procedure than given hitherto (and which may be significantly shortened by the use of hydrogen peroxide instead of air as oxidizing agent) may also be used, virtually without change, for the preparation of the chloride, bromide, iodide, sulfate, selenate, and oxalate of the carbonatotetrammine series simply by using an equivalent amount of the corresponding cobalt(II) salt as starting material.

Procedure

One hundred grams of cobalt(II) nitrate 6-hydrate (0.344 mol) is dissolved in 100 ml. of warm water and added to a mixture of 200 g. of ammonium carbonate (2.08 mols) in 1 l. of water and 500 ml. of concentrated ammonia. The resulting liquid is oxidized by sucking air through the solution contained in two 1-l. suction flasks fitted with stoppers and glass air-inlet tubes reaching almost to the bottoms of the vessels.* After 2½ hours, when the oxidation is complete, the solution is evaporated on the steam bath to a volume of 500 ml. Any cobalt(III) oxide is filtered off while hot, and further evaporation to 350 ml. is carried out. During the course of the evaporation 50 g. of solid ammonium carbonate should be added in 5-g. portions at regular intervals.† The solution is next cooled in ice, filtered by suction, and the crystals pressed well dry. The crystals may be washed with 75 ml. of alcohol. The filtrate is evaporated down to 100 ml., with the addition of four 5-g. portions of ammonium carbonate, and more product is isolated as above. The first batch of product, 48 to 50 g., is analytically pure, but the second may be contaminated with a trace of carbonatopentamminecobalt(III) nitrate, which is

* A timesaving but more costly method of oxidation is to add 250 ml. of 3% hydrogen peroxide slowly to the well-stirred cobalt(II) ammine mixture. After standing 10 minutes the solution is evaporated as below. The yield is the same.

† The regular addition of the ammonium carbonate is emphasized.

18059

Chemical Abstracts

18060

Vol. 52

the unsym. compd. reacts more slowly. The trisulfonates hydrolyze rapidly, giving SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_4^{2-}$, and a little tetrasulfonate; azodisulfonate is an intermediate. Tetrasulfonate hydrolyzes only slightly. R. H. Jaquith

The stability of metal tetraethylenepentamine complexes. Charles N. Reilley and J. H. Holloway (Univ. of N. Carolina, Chapel Hill). *J. Am. Chem. Soc.* 80, 2917-19 (1958).—From potential-pH diagrams the stability consts. (pK) of the following metal ion complexes of tetrathiylenepentamine (I) were detd.: $\text{Hg}^{(II)}$, 27.7; $\text{Cu}^{(II)}$, 22.9; $\text{Ni}^{(II)}$, 17.8; Zn , 15.4; Cd , 14.0; $\text{Pb}^{(II)}$, 10-11; $\text{Mn}^{(II)}$, 7.0; $\text{Bi}^{(III)}$; Ca , Mg , Sr , Ba , Al , and La , all negligible. pK values of 2-5 for I were found to be 4.1, 8.2, 9.2, and 10.0, resp., at 25° and with an ionic strength of 0.10. Analytical applications for I complexes are discussed. Gerald S. Golden

Arsenic(III) oxychloride, a new type of polymer bond. B. Thilo and P. Flögl (Akad. Wissenschaften, Berlin-Adlershof). *Angew. Chem.* 69, 754 (1957) (in German).— As_2O_3 dissolves in AsCl_3 with formation of an amorphous, hard polymer which has the structure $\text{Cl}_2\text{AsO}[(\text{Cl})\text{AsO}]_n\text{AsCl}_3$. Rudolph J. Marcus

The synthesis of metal complexes. III. Synthesis of ethylenediaminetcarbamato, ammineoxalato, and ethylenediaminoxalato series of cobalt(III) complexes. Motohichi Mori, Muraji Shibata, Eishin Kyuno, and Koji Hoashiya (Univ. Kanazawa). *Bull. Chem. Soc. Japan* 31, 291-5 (1958); cf. *C.A.* 51, 5618t.—Three series of $\text{Co}^{(III)}$ complexes were systematically synthesized from the green soln. of potassium tricarbonatocobaltate(III) (I), by means of successive substitution of carbonate by other groups: blue $\text{K}[\text{Co}(\text{en})(\text{CO}_3)_2]\cdot\text{H}_2\text{O}$ (II); violet $\text{K}[\text{Co}(\text{en})(\text{CO}_3)_2]\cdot\text{H}_2\text{O}$ (III); $[\text{Co}(\text{en})(\text{CO}_3)\text{Cl}\cdot\text{H}_2\text{O}$ (IV); $[\text{Co}(\text{en})_2\text{Cl}_2\cdot 3\text{H}_2\text{O}$ (V); blue- $\text{K}[\text{Co}(\text{NH}_3)_2\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}$ (VI); violet- $\text{K}[\text{Co}(\text{NH}_3)_2\text{C}_2\text{O}_4]\cdot\text{H}_2\text{O}$ (VII); $[\text{Co}(\text{NH}_3)_2\text{C}_2\text{O}_4]\text{Cl}$ (VIII); $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$ (IX); blue $\text{K}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]\cdot\text{H}_2\text{O}$ (X); violet $\text{K}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2]\cdot\text{H}_2\text{O}$ (XI); and $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)_2]\text{Cl}\cdot\text{H}_2\text{O}$ (XII). Of these, the blue and the violet varieties are probably to be regarded as new complexes, stereoisomeric with each other. Through all the procedures a green cold soln. of I was used as starting material. I was prep'd. from 20 g. KHCO_3 , 10 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 5 ml. 30% H_2O_2 by the method described in the previous paper. To I was added 5 g. ethylenediamine carbamate (XIII), prep'd. by passing CO_2 into a cold aq. soln. of 70% ethylenediamine (XIV). The mixt. was placed in an ice bath for 20 min. until the green color changed to blue, and 20 ml. of abs. EtOH was added. Impure crystals sepd. and were filtered off and rejected; 50 ml. addnl. EtOH was added to the filtrate, and the soln. was kept at 0° for some time. Crystals of II were collected and purified by dissolving them in a min. amt. of cold H_2O and adding abs. EtOH ; 4 g. of pure II were obtained. To I was added 5 g. XIII as before and the mixt. was kept 20 min. at room temp. A violet soln. was obtained; 20 ml. EtOH was added and the soln. was stored overnight in the refrigerator. The resulting ppt. was recrystd. 3 times as before with cold H_2O and abs. EtOH to yield 6 g. III. IV was prep'd. by adding 10 ml. 70% XIV to I, heating the mixt. on a water bath until the soln. became reddish yellow. After cooling, 11 g. of crude product was collected and recrystd. from H_2O . V was prep'd. by adding 15 ml. 70% XIV, 3 g. KCl , and 1 g. active C to I. The mixt. was heated 80 min. on a water bath until the color changed to brownish yellow, after which C was filtered off. The filtrate was evapd. to half the initial vol., cooled, and the ppt. washed with EtOH and dried. The yield was 12 g. V. I contg. 10 g. powd. $(\text{NH}_3)_2\text{C}_2\text{O}_4$ was warmed to 70°; when the soln. became bluish, it was cooled in an ice bath to stop further reaction and 50 ml. EtOH was added. The soln. was allowed to stand 1 hr. and the resulting crude product was collected and repprd. twice from the cold soln. by addn. of EtOH . The final ppt., which was washed with EtOH and Et_2O in turn, yielded 7 g. VI. The starting materials, the same as for VI, remained on a water bath until the color turned blue and finally violet; then 80 ml. EtOH was added and the soln. kept overnight in a refrigerator. The violet ppt. was collected, dissolved in small amt. of cold H_2O , and the complex was twice repprd. by addn. of EtOH . After the product was washed with EtOH and Et_2O , it yielded 7 g. VII. Powd. $(\text{NH}_3)_2\text{C}_2\text{O}_4$ (5 g.) and 30 ml. concd. NH_4Cl were added to I, 2 g. KCl was added, and the mixt. was warmed at 80° until the soln. became pink. The soln. was

which were removed by filtration, and 20 ml. addnl. EtOH was added; the yield was 6 g. VIII. To a cold soln. of I was added 16 g. powd. $(\text{CO}_2\text{H})_2$ until a bluish green soln. was obtained. The soln. was kept at 60° as long as CO_2 was evolved and then was cooled, acidified with dil. AcOH , and 50 ml. EtOH was added. The yield was 12 g. IX, which was purified as usual. $\text{K}_2\text{C}_2\text{O}_4$ (5 g.) and 5 g. ethylenediamine oxalate, prep'd. by neutralizing 15 g. 70% XIV with 23 g. powd. $(\text{CO}_2\text{H})_2$ in the cold, were poured into a cold soln. of I. The mixt. was kept about 1 hr. at room temp. until the color became bluish violet, after which it was cooled, treated with a small amt. of EtOH to remove foreign salts, and the filtrate was further treated with EtOH to ppt. 3 g. X. The ppt. was purified by washing with EtOH and Et_2O . XI (7 g.) was synthesized in the same way as X, except that the mixt. was heated 1 hr. instead of being left at room temp. A mixt. of 6 g. $(\text{CO}_2\text{H})_2$, 2 g. KCl , and 18 ml. 70% XIV was added to I and the mixt. evapd. on a water bath until a crust formed on the surface. The soln. was cooled and the crystals were filtered and washed with EtOH and Et_2O , yielding 10 g. XII. R. E. Dunbar

The study of the Raman spectra of the system nitrosoyl sulfuric acid-sulfuric acid-water with a view of denitrating highly concentrated sulfuric acid. Arthur Simon and Horst Richter (Tech. Hochschule, Dresden, Ger.). *J. prakt. Chem.* [4], 5, 68-76 (1957).—Raman spectra of vacuum distd. H_2SO_4 were recorded with a 3-prism Zeiss spectrograph having a dispersion of 84./mm. at 4358 Å. and 12A./mm. at 4916 Å. HNO_2 was prep'd. from N_2O_3 and H_2SO_4 . The N_2O_3 content of the nitroso acid was detd. with a Lunge nitrometer and H_2SO_4 was also detd. by the Lunge method. In the production of H_2SO_4 from gypsum, nitroso acids occur which cannot be denitrated with SO_2 . With the aid of Raman spectra the conditions necessary for denitrating highly concd. H_2SO_4 can be established, and the reactions between the nitroso group and SO_2 can be clarified. The NO^+ frequency in the Raman spectrum decreases as the concns. of water and N_2O_3 increase. The decrease being smaller the lower the concn. of H_2SO_4 . It is shown that the depression is caused by HSO_4^- . H_2SO_4 molecules (mostly assoc'd. by H-bridges) shield the polarizing effect of the HSO_4^- on the NO^+ ion and thereby change its bonding condition. Attempts to denitrate show that the bonding condition of the NO^+ ions, characterized by the position of the Raman frequency, is decisive for the denitrability of nitroso acids. George Meister

The complex formed from cobalt hydrocarbonyl and butadiene. Hans B. Jonassen, Robert I. Stearns, Jouko Kenttämäki, Donald W. Moore, and A. Greenville Whittaker (Tulane Univ., New Orleans, La.). *J. Am. Chem. Soc.* 80, 2586-7 (1958).—The complex formed between butadiene and Co hydrocarbonyl in the absence of Oxo conditions was prep'd. and the stereochem. configuration was studied. When K cobaltcarbonylate was allowed to react 12 hrs. with AcOH and liquid butadiene in a high-pressure vessel a red-brown liquid was obtained, b. 33-5° at less than 1 mm., and having the compn. $\text{Co}(\text{CO})_4\text{C}_4\text{H}_6$. It is diamagnetic and contains no acidic H. The infrared and ultraviolet absorption curves indicate the disappearance of the conjugated diolefin structure and the appearance of a structure producing absorption characteristics similar to those of cis monobenfins. The sharp peak at 703 cm^{-1} , which in the Co hydrocarbonyl has been assigned to the H vibrations, also disappears. Felix Saunders

The interaction of ammonium and potassium hexabromosmiate(IV) and liquid ammonia at 25°. II. Ammonia soluble products. George W. Watt and Lauri Vaska (Univ. of Texas, Austin). *J. Inorg. & Nuclear Chem.* 6, 246-51 (1958); cf. *C.A.* 52, 8819a, 12642h.—Reaction of K_2OsBr_6 and liquid NH_3 at ~25° gives $\text{NH}_3\text{-sol. } \mu\text{-nitridobis-[dibromotetrammineosmium(IV)] triiodidobromide}$. This was isolated as the 3-hydrate and converted to $\mu\text{-nitridobis-[dibromotetrammineosmium(IV)] triiodidobromide}$. When $(\text{NH}_3)_2\text{OsBr}_6$ accompanied by NH_3Br is allowed to react similarly, hexammineosmium(III) bromide is produced by reaction of NH_3Br and accompanying hexammineosmium(III) hexabromosmiate(III). Jack J. Bullof

The properties of calcium silicate hydrates. T. M. Berkovich, D. M. Khlebst, O. I. Gracheva, L. S. Zevin, and N. I. Kupreeva. *Doklady Akad. Nauk S.S.R.* 120, 868-8 (1958).—Ca silicate hydrates $\text{Ca}_2\text{Si}_2\text{H}_6$ ($\text{C} = \text{CaO}$, $\text{S} = \text{SiO}_4$, and $\text{H} = \text{H}_2\text{O}$) were synthesized. X-ray powder

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